



TITLE:

Study on Surface Electricity. (XIX) Capacity Measurement of Dropping Mercury Electrodes by Resonance Method. (1)

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thickness mode. In the third resonance, although comparatively strong vibration is excited as is presumed from the measurement of motional admittance, it is not desirable to use this resonance for the acoustic purpose, because the amplitude distribution is complicated and the directional characteristics of vibrator suffer harmful influences by the existence of the part of inverse phase on a radiating surface. It is concluded that the second resonance is the most effective among them.

6. Study on Surface Electricity. (XIX)

Capacity Measurement of Dropping Mercury Electrodes by Resonance Method. (1)

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As the interfacial phase between mercury and electrolytic solution is considered to be equivalent to an A. C. element containing a capacitance, a resonant circuit is constructed by connecting it with an inductance. This circuit satisfies the resonance condition when the following equation exists,

$$f = 1/(2\pi\sqrt{LC})$$

where f is the frequency, and L and C are the inductance and capacitance, respectively.

The interfacial area of a dropping mercury electrode increases continuously with time, which can be represented by

$$A = 4\pi \left[\frac{3mt}{13.6 \times 4\pi} \right]^{\frac{2}{3}},$$

where A is the interfacial area, m the rate of flow of mercury (g./sec.) and t is time. As the (differential) capacity per unit interfacial area takes its unique value (at a given polarization), the total capacitance of the interface increases with time, i. e.

$$C = C_0 A = C_0 k t^{\frac{2}{3}},$$

where C is the total capacitance, C_0 the specific capacity per unit area and k is constant for a given value of m .

Combining this equation and the above condition for resonance, we can conclude that, by choosing proper A. C. frequency and inductance, the circuit resonates at some instance during the growth of the mercury drop. The resonance curve can be reproduced on the screen of a cathode ray oscilloscope by applying the A.C. voltage occurring at the two terminals of the dropping electrode cell as the vertical axis and a

synchronized saw-tooth sweep voltage wave as the horizontal axis.

It is clear from the resonance condition that the resonant capacitance increases with decreasing the inductance at a given frequency, and we can, therefore, determine the point where the circuit resonates at the moment just before the drop falls. From this value and drop weight, we can easily calculate the specific (differential) capacity per unit area.

Now, the interfacial phase is not equivalent to a simple condenser, but shows several absorption phenomena, which are due to the solution resistance, leakage and the mechanical work of "Counter U-effect", etc. Representing them formally by a series resistance R_{eq} , we can define the "Q-factor" of this circuit by

$$Q = 1/(2\pi f R_{eq} C).$$

From simple calculation this value is shown to be equal to the ratio of the resonant voltage and the applied voltage, which can easily be observed from the amplifier readings.

7. Study on Surface Electricity. (XX)

Capacity Measurement of Dropping Mercury Electrodes by Resonance Method. (2)

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The structure of an interfacial double layer is controlled by the applied D. C. polarizing potential and the nature of the ions in solution. One of the most powerful means for studying the ionic behavior in this layer is the determination of the electrical capacity of dropping mercury electrodes. We have made this measurement for several salt solutions by the method described in the preceding article.

The typical shape of the specific capacity per unit area viz. polarizing potential (against electrocapillary maximum potential, i.e. the potential where the electronic charge of mercury surface is zero) is given in Fig. 1. In general, the capacity at anodic polarization is larger than that at cathodic side, which is considered to be due to the fact that anions are generally more easily dehydrated and approach nearer to the mercury surface than cations. The steep rise at extreme cathodic polarization is due to the reversible electrolysis ("pseudo-capacity"). There is a hump near electrocapillary maximum, but in the case of iodides and carbonates we can not find it.

Comparing the shapes of this curve for different electrolytic solutions we can